The Care and Feeding of Electrodes

BACKGROUND: The microstructure, cleanliness and chemical composition of the electrode surface determines how an electron-transfer reaction proceeds. Although a half-cell reaction of an oxidized species, Ox, being reduced to species R, looks simple

$$Ox \ + \ e\text{-} \ = \ R$$
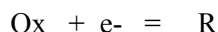
the actual process is much more complex. Let us imagine that you can sit as an observer on the electrode surface and look out into the solution. What you would see, ignoring for the moment the composition of the electrode surface except to say that it is electrically conductive, is solvent molecules. If the solvent is water, its molecules will appear to be moving in and out, but most will seem to be staying at the surface with a preferred orientation. Besides water, cations or anions of the electrolyte are present and some may be adhering to the surface, competing with the water molecules. Assuming that you also have Ox species in the solution, Ox being less numerous due to its lower concentration may also be observed, albeit less frequently than other components, near the electrode surface. When species stick on the surface, we call it adsorption, and the extent with respect to its bulk concentration, is described by an adsorption isotherm. The amount adsorbed will go to a maximum at monolayer coverage or saturation. If you peer out at a distance beyond a few layers of water, species will be seen to be moving at random except when electrolysis consumes Ox and mass transfer of Ox from the bulk solution occurs to replace the depleted Ox species adjacent to the electrode with R being produced. It in turn diffuses out to the bulk solution where its concentration is zero. It is a very dynamic process.

What happens at atomic dimensions in the first layer or so of the solution next to the surface of the electrode depends on the value of the applied potential (with respect to the reference electrode) and on the chemical composition and structure of the surface. At some value of the applied potential, there is no net positive (+) nor negative (-) charge on the electrode surface. The applied potential at which this occurs is referred to as the potential of zero charge, E_{pzc}. Water molecules will orient themselves with the negative end of the dipole (oxygen) toward the electrode when the potential is positive of E_{pzc} and visa-versa when it is negative. Similarly, there will be an excess of anions to neutralize the charge when the surface has excess + charge and again, excess of cations when negative. This excess of cations or anions decreases very rapidly with distance as we move away from the electrode to the bulk solution. This region next to the electrode where excess charge may be contained is referred to as the double layer. We can determine the double layer charge as the applied potential is changed from one value to another by integrating the current that flows. For details, the reader is referred to references [Refs. 1-3] and the experiment titled, Chronoamperometry, in this eChem Manual. To address the issue of the chemical composition and structure of an electrode surface and how these can affect the electrode reaction will be illustrated next by discussing what happens at a Pt electrode.

Platinum Electrode: How its chemical composition affects electrochemical reactions.
Pt is a noble metal that is very stable and resistant to corrosion. Because of its stability, like Au, it is often used to make jewelry. As an electrode, it is used to oxidize organics or to generate hydrogen or reduce

oxygen. You can order Pt as a wire of various diameters or foil with different thicknesses. Cypress/ESA sells Pt disk electrodes encased in glass or PEEK polymer with tip diameters of 1 mm and 10 um. These contain polycrystalline Pt, not single crystals, so the atoms are not arranged with a defined crystalline structure. Often, Pt electrodes contain a small amount of rhodium to give rigidity, especially when the electrode is a thin foil.

Figure 1 shows the cyclic voltammogram of a smooth Pt electrode in 0.5 M H_2SO_4 . Usually, *initial CVs* do not show such well-defined peaks or waves as seen in this figure. After many repetitive cycles, the peaks will begin to emerge as the surface is cleaned, and will go to a steady-state voltammogram. In the potential region of 0.4 to 0.8 (vs. NHE), the Pt surface is "clean" and the current flows to charge the double layer. As the potential goes more positive, the current is attributed to the formation of adsorbed oxygen or platinum oxide. The potential indicated by "2" is the start of bulk oxygen evolution. As the potential scan is reversed, the cathodic current is attributed to the reduction of surface platinum oxide. If there is dissolved oxygen in the solution, it will be reduced in this potential region concurrently with the reduction of platinum oxide. Scanning through the double layer region, the peaks due to adsorbed H-atoms are seen, where the shape, size and number of peaks depends on the crystal faces of the Pt surface. Bulk hydrogen evolution begins at "1." These surface processes are pH dependent with the cyclic voltammogram shifting by -60 mV per unit pH. The integrated charge under the H-atom adsorption peaks is said to be a good indicator of how many "clean" Pt atoms are on the surface and thus, a determinant of the surface area of active Pt [ref. 4]. Reference #4 is an excellent source to learn about chemisorption processes at solid electrodes.
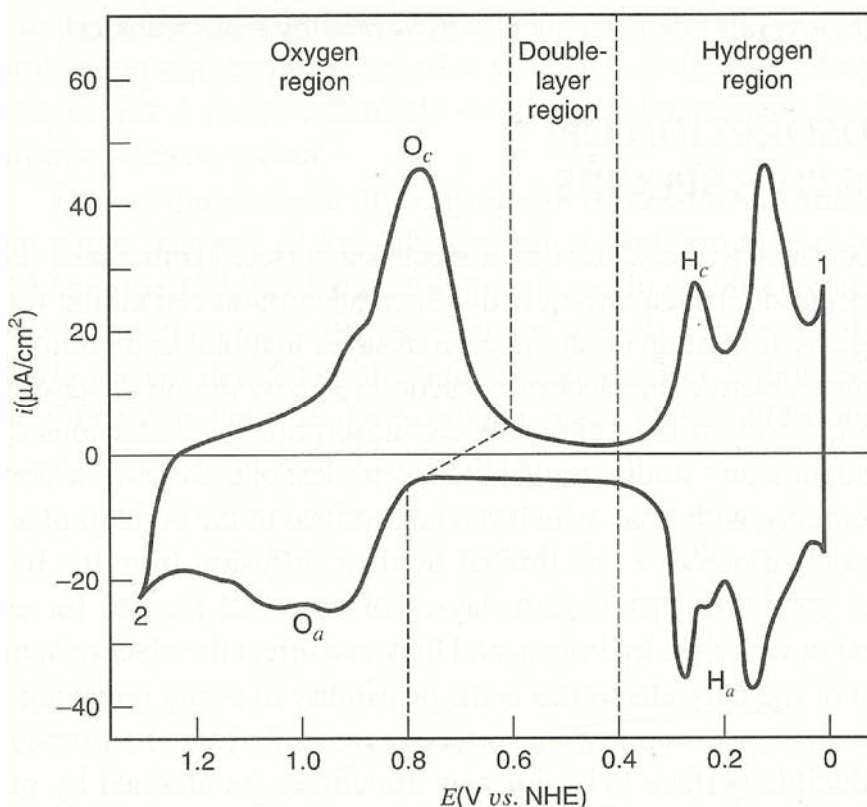

Figure 1. Cyclic voltammogram for a smooth Pt electrode in 0.5 M H2SO4. The various regions are discussed in the text. The shape, number and size of the peaks depend on the pretreatment of the electrode, solution impurities and supporting electrolyte. Reprinted with permission from A. J. Bard and L. Faulkner in Electrochemical Methods: Fundamentals and Applications, 2nd Ed., J. Wiley & Sons. Copyright J. Wiley & Sons 2001.

Surface cleanliness is a major issue with all electrodes. Pt is unique in that the surface impurities can be removed by repetitive scanning through a potential region where the impurities can be oxidized or removed into solution as platinum oxide is reduced. In the double-layer region, the high surface activity of Pt, due to its atoms having unfilled d-orbitals, can be used advantageously to detect analytes eluted in liquid chromatography utilizing a technique called "pulse amperometric detection (PAD)" [ref 5]. PAD is a pretty neat idea. Analytes (e.g. aliphatic amines, carbohydrates and alcohols) that normally are not considered electroactive are adsorbed onto the clean Pt surface while the applied potential is held in the double layer region. The potential is then stepped to a value in the Pt oxide region and there is concurrent oxidation of the adsorbed species and Pt oxide formation. The difference in the current or the integrated charge can be related to the amount of analyte, after subtraction of the background, which is obtained from an experiment without the presence of the analyte in solution. The potential is then stepped to the H-atom region to clean the electrode; i.e., to reduce the Pt oxide and remove any impurities that may be on the surface from the oxidation of the analyte. The process is then repeated to get some statistics on the process. The PAD analysis relies on the amount of analyte adsorbed being proportional to the concentration in solution, and the analyte not catalytically oxidized (dehydrogenated) by clean Pt. In the latter case, Johnson and LaCourse have developed innovative PAD procedures to accommodate the different mechanisms seen with various analytes, particularly with Au electrodes [ref. 6, 7].

PAD is one illustration of how the surface chemistry plays an important role and can be advantageously utilized for electro analytical purposes.

Activation of Pt Electrode

There are various ways to activate a Pt electrode. Although cleanliness is important, it is nearly impossible to avoid impurity adsorption unless the entire process is conducted in a sealed high vacuum chamber where the surface is cleaned by ion or electron bombardment. To preserve the cleaned surface, it is necessary to transfer the electrode to a cell containing the solution in the vacuum chamber. Not an easy task and one that requires specialized equipment and training. One method in the laboratory is to repetitively CV cycle the Pt electrode from –0.2 V to +1.0 V vs. Ag/AgCl reference electrode in 1 M H_2SO_4 until well-defined H-adsorption waves appear. High purity water must be used for making solutions and for best results, the solution degassed by purging with pure N_2 or argon to remove oxygen, and maintaining a flow of the gas above the solution during experiments.

Just remember, when you use solid electrodes like Pt, the surface chemistry can greatly affect what you see for the electrochemistry of the analyte.

Activation of Glassy Carbon Electrodes

Carbon-based electrodes are nearly ubiquitous in the laboratory today because of their availability in various forms and shapes, and usefulness over a wide potential range. There are various compositions of carbon, ranging from highly ordered pyrolytic graphite to less ordered glassy carbon to boron doped diamond to carbon-paste to exquisitely small carbon nano-tubes. Rick McCreery has written a comprehensive report on carbon electrodes, their surface properties and applications [ref. 8]. The most commonly used carbon-based electrode in the analytical laboratory is glassy carbon (GC). It is made by pyrolyzing a carbon polymer, under carefully controlled conditions, to a high temperature like 2000 ^{o}C. An intertwining ribbon-like material results with retention of high conductivity, hardness and inertness. The electrochemistry is affected greatly by its surface chemistry of carbon-oxygen functionalities and its cleanliness; i.e., absence of adsorbed impurities. This latter has been shown by McCreery and coworkers who cleaned and stored GC in solutions containing highly adsorbing carbon particles that preferentially removed impurities [ref. 9].

We will focus on GC and discuss methods of surface activation and maintenance of surface cleanliness. For analytical purposes, Cypress/ESA offers GC disk electrodes of 3 mm diameter encased in glass or 10 um and 1 mm disks encased in PEEK polymer.

The most common method of activation is to polish the GC surface with micro-sized abrasives. Such treatment exposes fresh new surface. The maintenance of clean conditions during such polishing is critical. For instance, polishing on some types of abrasive containing pads can deactivate the surface [ref. 10]. After polishing, sonication is often required to remove carbon particles and remains of polishing material. These steps may be time consuming and repeated sonication may eventually destroy the electrode by compromising the seal between the carbon and the outer cladding material (e.g., glass or PEEK). Use of large agglomerated particles for polishing may leave large surface scratches and indentations. The best activation procedure may be vacuum heat treatment (VHT) [ref.11] although polishing with alumina in cyclohexane may yield comparable active GC electrodes [ref. 9]. An interesting feature about VHT and the use of an organic solvent for polishing, are the absence or low oxygen-containing functionalities on the carbon surface. Chen and McCreery [ref. 12] has nicely addressed how and when such functionalities affect electron transfer processes.

In this TechNote a simple method is described on how to activate a Cypress System glassy carbon (GC) electrodes that produces a smooth surface with a high degree of activation. In addition, we demonstrate a method to keep the electrodes active during storage or between experiments to minimize need for repolishing.

Procedure
Polishing on smooth ground glass plates allows the condition of the polishing material to be tightly controlled for optimum cleanliness. In addition, the use of deagglomerated alumina of small particle size (0.05 μm) allows for a more scratch free active electrode surface. The use of particles of even smaller size (0.007 μm fumed silica) should enhance the smoothness and activity. If this does not activate the surface, re-polishing with larger particle size abrasive, such as 0.25 :m diamond, followed by 0.05 :m alumina or 0.007 :m silica.

Materials
   * 1 mm diameter (or larger) GC disk electrode
   * Ag/AgCl reference electrode
   * NANOpure^{TM} deionized water
   * Baikalox agglomerate free alumina, 0.05 μm particle size (Baikowski International, Charlotte, NC) or Buehler 0.05 μm alumina
   * Fumed Silica 0.007 μm particle size (Sigma, St. Louis, MO)
   * Smooth ground glass plate (necessary to prevent scratches during polishing)

How to polish your electrodes: The degree of activation of a GC disk electrode can be evaluated by looking at the difference in the peak potential for the redox couple of ferri/Ferrocyanide, which is expected to be close to 60 mV [9]. First, use a slurry of the 0.05 μm alumina to polish the electrode. You can add several scoops of alumina to a small wash bottle of high purity water, like Nanopure^{TM}, and squirt it on a clean ground glass plate. For optimum cleanliness it is wise to use gloves when handling the electrodes. This precaution is necessary so that skin oils do not get onto the electrode. Polish with light pressure following a figure 8 pattern for approximately 30 seconds. The electrode should then be immediately rinsed with water. It is suggested that the stream of water be directed against the surface of the electrode. Only high purity water is used throughout the activation process. In order to remove excess water, touch the outer edge of the electrode with a soft tissue paper like Kimwipe^{TM}.

Now check the activation of the electrode in a solution 1 mM ferrocyanide in 1 M KCl. Be sure to degass all solutions with high purity nitrogen or argon before running the experiment. A typical result for an electrode scanned at 100 mV/s is shown in Figure 2. For this electrode $\Delta E_p = 67$ mV is very close to the expected result.

It is recommended that any further polishing of the electrode be done in a slurry of 0.007 µm fumed silica. Thoroughly wash the polishing plate with water, dry with a Kimwipe[TM] and add a small amount of silica onto the polishing plate. Add a small amount of water to make a slurry. The silica should be visibly white on the plate. The electrode can be polished for 30 seconds in a figure 8 pattern, cleaned with pure water and then the outer edge of the electrode barrel be touched with Kimwipe[TM] to remove excess water. If your electrode does not produce satisfactory results, repeat the process.

How to keep your electrodes active
GC electrodes can retain much of their activity by storing them in a solution of alumina or silica. To do this, add 6 or 7 scoops of either alumina or silica to about 25 ml of deionized water and stir the solution with the electrode in it. Essentially, the electrode is being continuously polished. When you are ready to use the electrode again, rinse it with a stream of pure deionized water and it is ready to go. The CV data for ferrocyanide oxidation, as a result of storing GC in alumina and silica, are tabulated in Table 1 and CVs are shown in Figures 3 and 4, respectively. Electrodes stored overnight in alumina or silica maintained a much higher degree of activation than when left exposed to air.

Table 1: Results of storing GC electrode in Solutions of Alumina or Fumed Silica

Stored in Alumina

	ΔE_p, mV
a) Polished with alumina	72
b) Stored overnight in stirred alumina	103
c) Exposed to lab air for 4 hrs	144

Stored in Silica

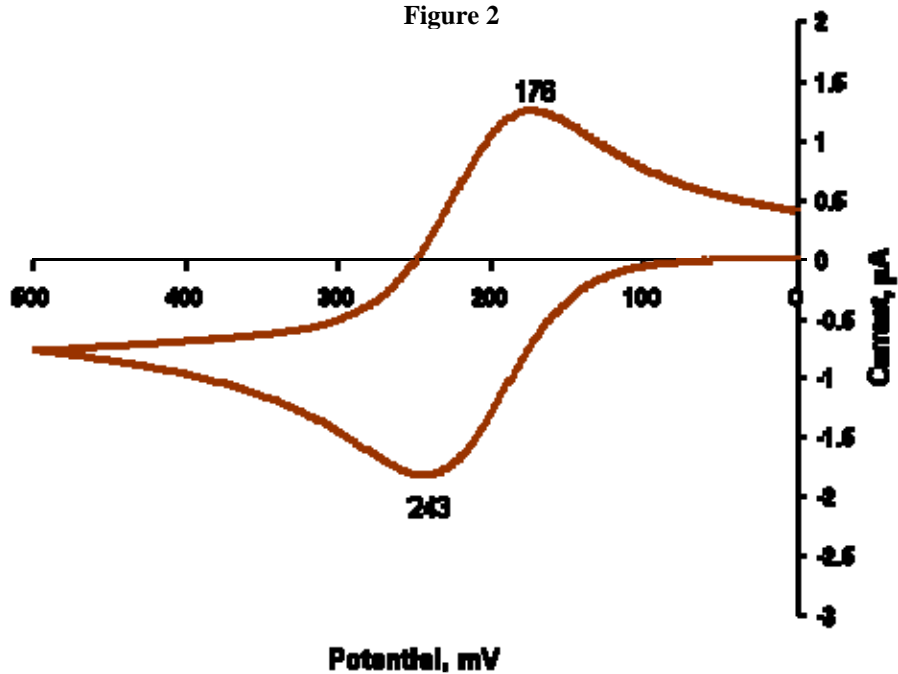|	ΔE_p, mV
a) Polished with Silica	75
b) Stored overnight in stirred silica	123
c) Exposed to lab air for 4 hrs	195

Figure 2

Figure 2. Cyclic voltammogram of 1 mM ferrocyanide in 1 M KCl with a freshly polished glassy carbon electrode.
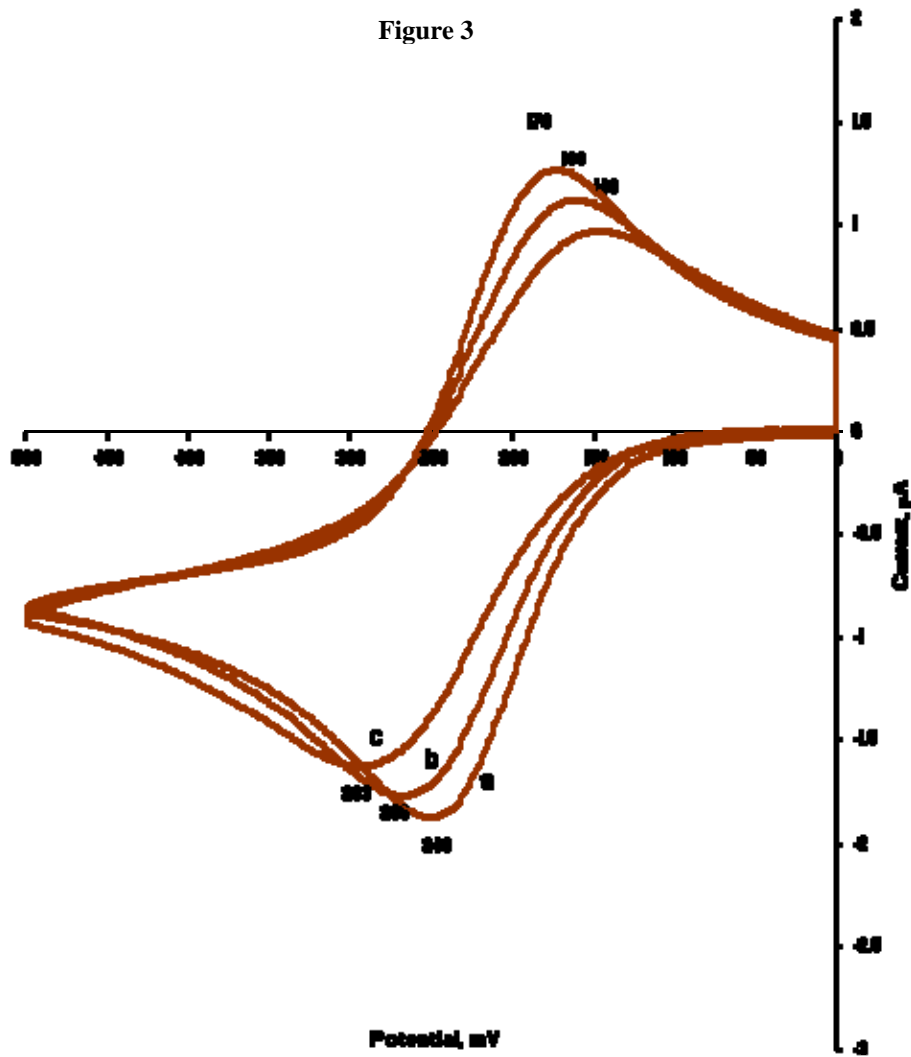
Figure 3

Figure 3. CV of 1 mM ferrocyanide in 1 M KCl a) with a freshly polished GC,
b) after storage overnight in alumina, and c) after exposure to air for 4 hours.
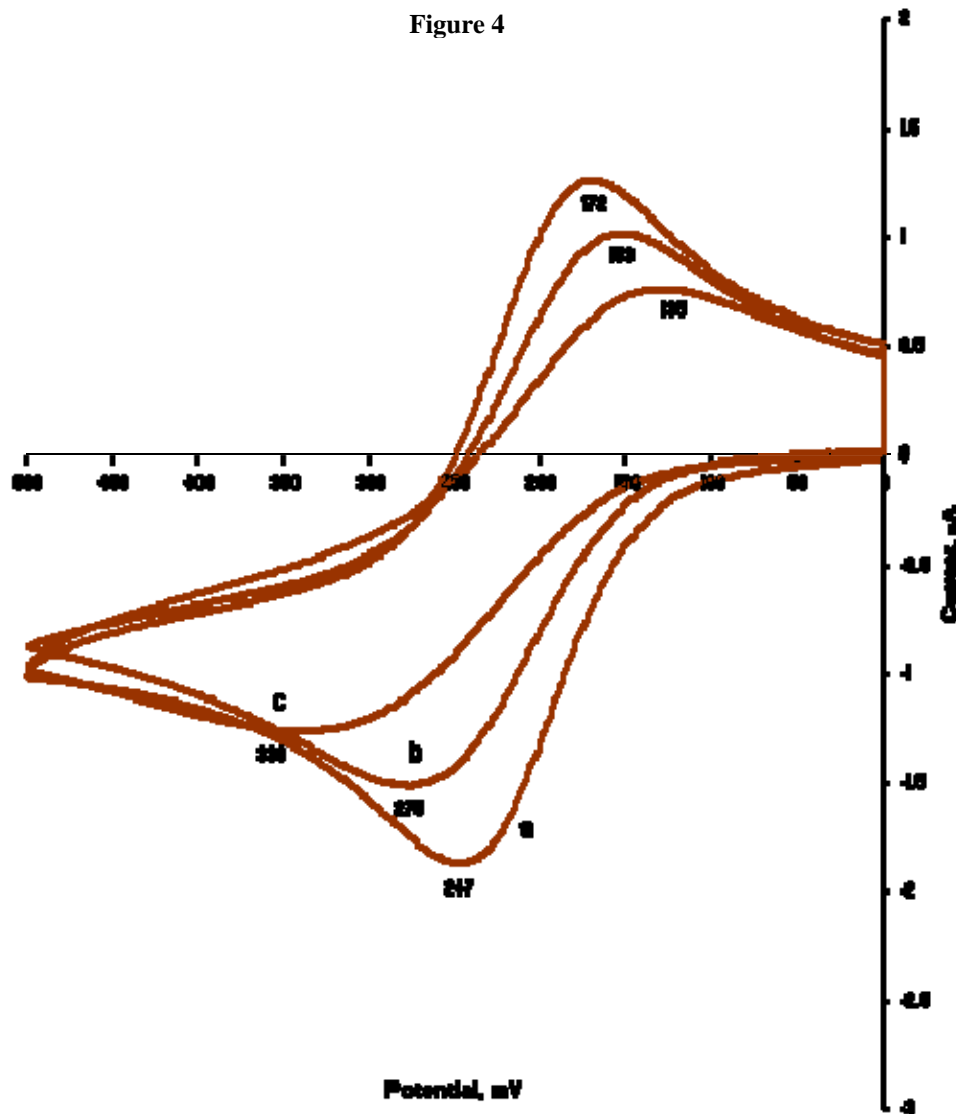
Figure 4

Figure 4. CV of 1 mM ferrocyanide in 1 M KCl with a) freshly polished GC, b) stored
overnight in silica, and c) after exposure to lab air for 4 hours.

Conclusions

A simple, quick and inexpensive method for pretreating GC disk electrodes without use of sonication has
been demonstrated. The resulting electrodes have nearly reversible appearing CVs with the difference
between the peak potentials near the theoretical value of 60 mV. In fact, this technique gives comparable
results to more time consuming and complex techniques requiring multiple polishing and sonication (Δ
Ep= 67.7 mV and 121 mV), or vacuum heat treatment (ΔEp= 64.5 mV and 64 mV) [Refs. 10, 11]. In
addition, a method has been described for retaining electrode activity for several hours (at least overnight)
without polishing.

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